LUBRICANT ADDITIVES

CHEMISTRY AND APPLICATIONS

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Detergents

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1 INTRODUCTION

Modern equipment must be lubricated in order to prolong its lifetime. A lubricant* performs a number of critical functions. These include lubrication, cooling, cleaning and suspending, and protecting metal surfaces against corrosive damage [1]. Lubricant comprises a base fluid and an additive package. The primary function of the base fluid is to lubricate and act as a carrier of additives. The function of additives is either to enhance an already-existing property of the base fluid or to add a new property. The examples of already-existing properties include viscosity, viscosity index, pour point, and oxidation resistance. The examples of new properties include cleaning and suspending ability, antiwear performance, and corrosion control. The extent of the desirability of various properties differs from lubricant to lubricant and largely depends on the conditions of use. Automotive use, for example, requires lubricants with good oxidation resistance, suitable low- and high-temperature viscosities, high-viscosity index (i.e., minimum loss in viscosity with an increase in temperature), and good cleaning and suspending ability. Conversely, the use as nonautomotive lubricants, such as industrial and metal-working lubricants, emphasizes oxidation resistance, antiwear performance, corrosion control, and cooling ability.

One of the most critical properties of the automotive lubricants, especially engine oils, is their ability to suspend undesirable products from thermal and oxi-

*The terms "lubricant" and "oil" are interchangeable and are different from the terms "base oil" and "base fluid". Lubricant and oil imply base oil or a base fluid plus additives.

dative degradation of the lubricant. Such products form when the byproducts of fuel combustion, such as hydroperoxides and free radicals, go past piston rings into the lubricant and, being reactive species, initiate lubricant oxidation. The resulting oxidation products are thermally labile and decompose to highly polar materials with a tendency to separate from the bulk lubricant and form surface deposits and clog small openings. The former will lead to malfunctioning of the closely fitted surfaces, such as those between pistons and cylinder walls, and the latter will impair oil flow to parts needing lubrication. The separation tendency of these products relates to their high polar–nonpoplar ratio [2], which makes them less soluble in largely nonpolar base oil. A lubricant with high-oxidation resistance, due to the quality of the base fluid and/or the presence of a good oxidation inhibitor additive package, will slow down the formation of these undesirables.

Oxidation inhibitors, detergents, and dispersants make up the general class of additives called *stabilizers and deposit control agents*. These additives are designed to control deposit formation, either by inhibiting the oxidative breakdown of the lubricant or by suspending the harmful products already formed in the bulk lubricant. Oxidation inhibitors intercept the oxidation mechanism, and dispersants and detergents perform the suspending part [3, 4]. *Detergents* are the topic of this chapter, and *dispersants* are the topic of the subsequent chapter. Detergents are metal salts of organic acids that frequently contain associated excess base, usually in the form of carbonate. Dispersants are metal-free and are of higher molecular weights than detergents. The two types of additives work in conjunction with each other.

The final products of combustion and lubricant decomposition include organic and inorganic acids, aldehydes, ketones, and other oxygenated materials [4, 5]. The acids have the propensity to attack metal surfaces and cause corrosive wear. Detergents, especially basic detergents, contain reserve base that will neutralize the acids to form salts. While this decreases the corrosive tendency of the acids, the solubility of the salts in the bulk lubricant is still low. The organic portion of the detergent, commonly called "soap", has the ability to associate with the salts to keep them suspended in the bulk lubricant. However, in this regard, detergents are not as effective as dispersants because of their lower molecular weight. The soap in detergents and the dispersants also have the ability to suspend nonacidic oxygenated products, such as alcohols, aldehydes, and resinous oxygenates [4]. The mechanism by which this occurs is depicted in Figure 1.

Dispersants and detergents together make up the bulk, about 45–50%, of the total volume of the lubricant additives manufactured. This is a consequence of their major use in engine oils, transmission fluids, and tractor hydraulic fluids, all of which are high-volume lubricants [6].

As mentioned, detergents neutralize oxidation-derived acids as well as help suspend polar oxidation products in the bulk lubricant. Because of this, these additives control rust, corrosion, and resinous buildup in the engine. Like most additives detergents contain a surface-active polar functionality and an oleophilic hydrocarbon group, with an appropriate number of carbon atoms to ensure good oil solubility [2]. Sulfonate, phenate, and carboxylate [7] are the common polar groups present in detergent molecules. However, additives containing salicylate and thiophosphonate functional groups are also sometimes used.

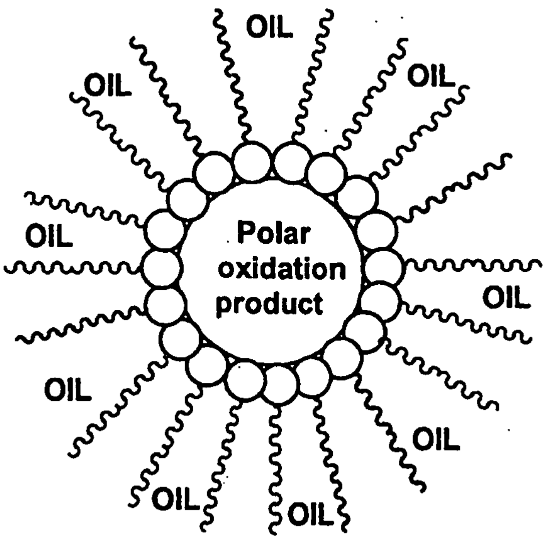

Figure 1 Oil suspension of polar oxidation products.

2 DETERGENT TYPES

Detergents are the metal salts of organic acids. The acids normally used to synthesize these compounds include arylsulfonic acids, such as alkylbenzenesulfonic acids and alkylnaphthalenesulfonic acids [8–11]; alkylphenols [12–16]; carboxylic acids, such as fatty carboxylic acids, naphthenic acids, and petroleum oxidates [17–20]; and alkenylphosphonic and alkenylthiophosphonic acids [21–23]. Sometimes a mixture of different types of acids is also employed [24]. The reaction of these acids with inorganic bases, such as metal oxides, metal hydroxides, and metal carbonates, results in the formation of salts [7]. The quantity of the metal used may be equal to (stoichiometric amount) or in excess of the exact amount necessary to completely neutralize the acid functionality. The presence of metal in stoichiometric amount results in the formation of the neutral salt, often referred to as a neutral detergent or soap. If the metal is present in excess, the detergents are called *basic*, *overbased*, or *superbased* [7, 25]. It is important to note that basic detergents appear as clear homogeneous fluids, the same as neutral detergents, because the excess metal is present in a colloidal form [26]. The general formulas for metal sulfonates, metal phenates, and metal carboxylates are presented in Figure 2.

$(RSO_3)_a M{\cdot}xM_bCO_3{\cdot}yM(OH)_c$

Basic Sulfonate

$(RPhO)_aM{\cdot}xM_bCO_3{\cdot}yM(OH)_c$

Basic Phenate

$(RCOO)_aM{\cdot}xM_bCO_3{\cdot}yM(OH)_c$

Basic Carboxylate

a and $c = 1$ and $b = 2$, if the metal **M** is monovalent; a and $c = 2$ and $b = 1$, if the metal **M** is divalent.

Figure 2 General formulas for detergents. (From Ref. 6.)